Computer simulation of aromatic polyesters including molecular dynamics

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A theoretical analysis of the possible conformations of poly(*p*-phenylene terephthalate) (PPTA) and poly(*p*-phenylene isophthalate) (PPIA) is performed on the basis of molecular mechanics and molecular dynamics trajectories. An algorithm for creating long polymer chains up to 150 monomers used for the calculation of the small-angle X-ray form factor is introduced. Three different methods to determine the experimentally accessible property, persistence length, are presented. The results of all three methods agree very well with the experimental result for the persistence length of PPTA; in addition, the relationship between stiffness and persistence length is elucidated by comparison of the two different conformations of PPTA and PPIA.

(Keywords: aromatic polymer; polyesters; computer simulation; molecular dynamics; conformations)

INTRODUCTION

The aromatic polyester poly(*p*-phenylene terephthalate) (PPTA) belongs to the class of stiff polymers[1]. As a measure of stiffness, quantities like the root-mean-square radius of gyration, the characteristic ratio or the persistence length are used. For the case of poly(*p*-hydroxybenzoic acid) esters, it has been shown[2] that these quantities depend strongly on the size of the fluctuations of the torsional angle around the ester bonds. In this paper the dependence of the persistence length on these fluctuations is discussed for PPTA in the frame of the rotational-isomeric-state (RIS) model[3]. Realistic parameters like bond lengths and bond angles are provided by computer simulations using molecular dynamics. Comparison is made by calculating the persistence length. Poly(*p*-phenylene isophthalate) (PPIA) is not a linear chain in the sense of the topological shape of the initial conformation (see *Figure 2*) and so we expect comparatively small values for the persistence length. For this type of chain quantities like the persistence length are obviously not a good measure for stiffness, as will be discussed in detail for PPIA in this paper.

Because of the limitation of computer time, computer simulations are restricted to the treatment of rather short chains. In order to work with longer chains an algorithm was developed which creates arbitrarily long chains using parameters that may be taken from molecular dynamics simulations. With the help of this algorithm small-angle X-ray scattering form factors are calculated, and so another bridge to experiment is built up.

THEORY

Molecular dynamics simulations

For the molecular dynamics the AMBER code[4] was used, which integrates Newton's equations of motion numerically by applying the leap-frog algorithm[5]. Small finite time steps ($\Delta t = 0.5 \times 10^{-15}$ s) assure a reliable representation of the trajectory. The interacting forces are calculated as the gradient of a potential given by:

$$V = \sum_b f_b(r_b - r_{b,\mathrm{eq}})^2 + \sum_v f_v(\delta_v - \delta_{v,\mathrm{eq}})^2 + \sum_d f_d[1 + \cos(n_d\phi_d - \delta_d)] + \sum_{i<j} \frac{1}{4\pi\varepsilon}\frac{q_i q_j}{r_{ij}} + \sum_{i<j} \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \qquad (1)$$

The single terms represent the potentials given by stretching of bonds, bending of bond angles, torsion of bonds, electrostatic interactions and van der Waals interaction. An 'all-atom' force field was used, i.e. the hydrogen atoms are explicitly considered. With the exception of the parameters concerning the explicit hydrogens and the partial charges, all the parameters are the same as in a previous paper[2], and are derived from microwave spectroscopy, neutron diffraction, molecular mechanical calculations, n.m.r. studies and crystal packing calculations. The partial charges are calculated by the MNDO (modified neglect of differential overlap) method[6] and are listed in *Table 1*.

The simulations were performed keeping the temperature constant. This is done by a 'coupling to a thermal bath'[7] incorporated in the AMBER code. Tracing the trajectory, the coordinates are stored and quantities like the persistence length can be calculated as time-averaged quantities.

Persistence length

The persistence length was calculated in three different ways.

(i) The RIS model requires knowledge of mean bond lengths and the mean sine and cosine of bond and torsional angles for all bonds. According to *Figure 1*,

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Table 1 Partial charges[a] of the atoms for PPTA and PPIA (numbers according to *Figure 1* and *Figure 2*, respectively)

PPTA		PPIA	
q_1	0.49	q_1	0.51
q_2	−0.47	q_2	−0.47
q_3	−0.12	q_3	−0.20
q_4	−0.05	q_4	0.04
q_5	0.15	q_5	0.14
q_6	−0.05	q_6	−0.16
q_7	0.15	q_7	0.13
q_8	−0.05	q_8	0.04
q_9	0.15	q_9	0.14
q_{10}	−0.05	q_{10}	0.07
q_{11}	0.15	q_{11}	0.17
q_{12}	−0.12	q_{12}	−0.20
q_{13}	0.49	q_{13}	0.51
q_{14}	−0.47	q_{14}	−0.47
q_{15}	−0.29	q_{15}	−0.31
q_{16}	0.07	q_{16}	0.07
q_{17}	−0.07	q_{17}	−0.07
q_{18}	0.13	q_{18}	0.13
q_{19}	−0.07	q_{19}	−0.07
q_{20}	0.13	q_{20}	0.13
q_{21}	−0.07	q_{21}	−0.07
q_{22}	0.13	q_{22}	0.13
q_{23}	−0.07	q_{23}	−0.07
q_{24}	0.13	q_{24}	0.13
q_{25}	0.07	q_{25}	0.07
q_{26}	−0.29	q_{26}	−0.29

[a] The partial charges are scaled by a factor of 1.3, the empirical value fitting the AMBER force field

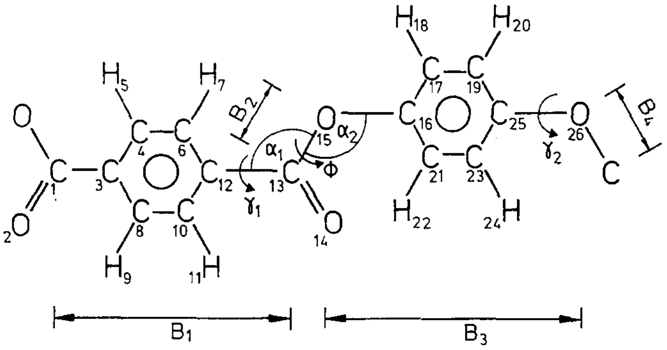

Figure 1 PPTA monomer unit (*cis–cis* conformation); the phenyl ring in the hydroquinone (HQ) residue is rotated about 90° around the O–O axis for the initial conformation

four bonds are needed for PPTA. The transformation matrices T_i are defined in such a way that T_i describes the averaged transformation of the components of the vector associated with bond $i+1$ (B_{i+1} in *Figure 1*) to the components of the vector associated with bond i (B_i). Matrix T_4 describes the transformation of B_1 to B_4. Regarding the symmetry of PPTA, the transformation matrices have the following form:

$$T_i = \begin{pmatrix} -\langle\cos\alpha_i\rangle & \langle\sin\alpha_i\rangle & 0 \\ -\langle\sin\alpha_i\rangle\langle\cos\phi_i\rangle & -\langle\cos\alpha_i\rangle\langle\cos\phi_i\rangle & 0 \\ 0 & 0 & -\langle\cos\phi_i\rangle \end{pmatrix} \qquad i = 1,\ldots,4 \quad (2)$$

where ϕ_i denote the torsional angles and α_i the bond angles. The mean values of cosine and sine are calculated by:

$$\begin{aligned} \langle\cos\delta\rangle &= \cos\langle\delta\rangle(1 - \tfrac{1}{2}\langle\Delta^2\delta\rangle) \\ \langle\sin\delta\rangle &= \sin\langle\delta\rangle(1 - \tfrac{1}{2}\langle\Delta^2\delta\rangle) \end{aligned} \qquad (3)$$

By taking the symmetry of the monomer into account we obtain:

$$\begin{aligned} \langle\alpha_1\rangle &= \langle\alpha_4\rangle \\ \langle\alpha_2\rangle &= \langle\alpha_3\rangle \\ \langle\phi_1\rangle &= \langle\phi_3\rangle = \langle\phi\rangle \\ \langle\phi_2\rangle &= \langle\gamma_1\rangle = 0^\circ \text{ or } 180^\circ \\ \langle\phi_4\rangle &= \langle\gamma_2\rangle = 0^\circ \text{ or } 180^\circ \end{aligned} \qquad (4)$$

All possible combinations of the values for $\langle\gamma_1\rangle$ and $\langle\gamma_2\rangle$ correspond to the four possibilities of a *trans–trans*, *trans–cis*, *cis–trans* and *cis–cis* conformation. Assuming equal probability for all of these conformations we get:

$$T_2 = \begin{pmatrix} \langle\cos\alpha_2\rangle & \langle\sin\alpha_2\rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
$$T_4 = \begin{pmatrix} \langle\cos\alpha_1\rangle & \langle\sin\alpha_1\rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (5)$$

The entire rotation matrix is given by:

$$T = T_1T_2T_3T_4 \qquad (6)$$

The vector characterizing a monomer is given by:

$$\mathbf{l} = l\hat{e}_l \qquad (7)$$

where $\hat{e}_l$ is the unit vector in the direction of $\mathbf{l}$ and l is the absolute value of $\mathbf{l}$.

The characteristic ratio is then given by[3]:

$$C_\infty = \hat{e}_l^{\mathrm{T}}(E+T)(E-T)^{-1}\hat{e}_l \qquad (8)$$

where E is the unit matrix of order 3. For chains consisting of different conformations (*cis–trans*, *trans–trans*, etc.), the formula above is not strictly correct, since in this case l is less than the average length of a monomer due to the specific form of T_2 and T_4 in equation (5).

A possible correction is given by:

$$C_\infty = \mathbf{l}^{\mathrm{T}}(E+T)(E-T)^{-1}\mathbf{l}/l'^2 \qquad (9)$$

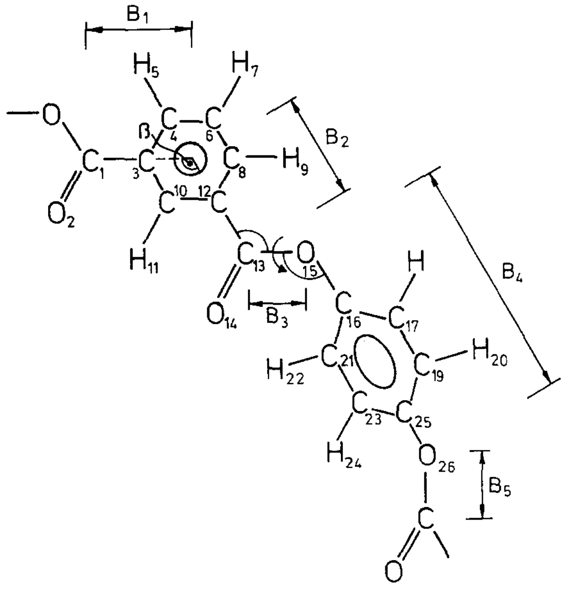

Figure 2 PPIA monomer unit (*cis–cis* conformation)

where l' is the monomer length taken directly from molecular dynamics. The persistence length is then given by[3]:

$$a = \tfrac{1}{2} l'(C_\infty + 1) \tag{10}$$

For PPIA five rotation matrices are required according to *Figure 2*. The additional transformation matrix T_1 (transforming B_2 into B_1) again allows two possible mean values for the torsional angle (0° or 180°) and consequently there are altogether eight possible conformations for one monomer. For PPIA randomly chosen, different monomeric conformations were simulated. The transformation matrices are then given by:

$$\begin{gathered}
T_1 = \begin{pmatrix} \langle\cos\beta\rangle & \langle\sin\beta\rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
T_2 = \begin{pmatrix} \langle\cos\alpha_1\rangle & \langle\sin\alpha_2\rangle & 0 \\ \langle\sin\alpha_1\rangle\langle\cos\phi\rangle & \langle\cos\alpha_1\rangle\langle\cos\phi\rangle & 0 \\ 0 & 0 & -\langle\cos\phi\rangle \end{pmatrix} \\
T_3 = \begin{pmatrix} \langle\cos\alpha_2\rangle & \langle\sin\alpha_2\rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
T_4 = \begin{pmatrix} \langle\cos\alpha_2\rangle & \langle\sin\alpha_2\rangle & 0 \\ \langle\sin\alpha_2\rangle\langle\cos\phi\rangle & \langle\cos\alpha_2\rangle\langle\cos\phi\rangle & 0 \\ 0 & 0 & -\langle\cos\phi\rangle \end{pmatrix} \\
T_5 = \begin{pmatrix} \langle\cos\alpha_1\rangle & \langle\sin\alpha_1\rangle & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}
\end{gathered} \tag{11}$$

The persistence length is calculated in the same way as for PPTA according to equations (6), (9) and (10).

(ii) The second method employs the accepted and usual definition of a wormlike chain. Under these assumptions the persistence length is calculated by:

$$a = \frac{-L}{\ln\langle\cos\omega\rangle} \tag{12}$$

where ω is the angle between the tangent vectors of two arbitrarily chosen points of the chain, L is the contour length between these points and a is the persistence length. Details for applying this method are found in a previous paper[2].

(iii) The third method is based on the well known relation between end-to-end distance and persistence length for a wormlike chain[8]:

$$\langle r^2\rangle = 2a[L - a + a\exp(-L/a)] \tag{13}$$

A similar relation can be found for a freely rotating chain, thus generalizing relation (13) for chains with real bonds:

$$\langle r^2\rangle = 2a\left\{nl - \frac{nl^2}{2a} - a\left(1 - \frac{l}{a}\right)\left[1 - \left(1 - \frac{l}{a}\right)^n\right]\right\} \tag{14}$$

where l is the monomer length and n the number of monomers. This formula takes the form of equation (13) in the continuous limit, i.e. $n \to \infty$, $1 \to 0$ and $L = nl =$ constant. Equation (14) is solved for a by an iteration procedure and gives in general higher values for a than equation (13).

SAXS form factors

In principle, comparison of computer simulations with experiments can also be made by calculating small-angle X-ray scattering form factors. In order to obtain the structure of the form factors it is necessary to treat long chains. A 'cheap' way to obtain long chains is the following. Average bond lengths, bond angles and torsional angles are taken from molecular dynamics simulations and then used to construct the transformation from one bond to the next one. This can be done in principle in the frame of the RIS model using transformations of the coordinate system for each bond, although for most applications it is easier to keep the coordinate system fixed and to employ active transformations. This is achieved by the formula[9]:

$$X' = X\cos\omega + \hat{\omega} \times X\cos\omega + (1 - \cos\omega)(\hat{\omega}\cdot X)\cdot\hat{\omega} \tag{15}$$

where $\hat{\omega}$ represents the unit vector in the direction of the rotation axis and ω is the corresponding rotation angle. In order to perform a complete transformation from bond i to bond $i + 1$, equation (15) has to be applied twice with appropriate rotation axes.

Bond angles and torsional angles are assigned values for each bond, which are randomly distributed around the mean values, obeying a normal distribution with a standard deviation also obtained from the molecular dynamics simulations.

The persistence length can be calculated directly as the average projection of the end-to-end vector onto the axis of the first monomer. Applying the Debye scattering relation for randomly oriented chains[10]:

$$I(s) \sim \sum_{i=1}^{n}\sum_{k=1}^{n} f_i f_k \frac{\sin(sr_{ik})}{sr_{ik}} \tag{16}$$

where n is the number of scattering centres, f_i their atomic form factors, r_{ik} the distance between them and $s = (4\pi/\lambda)\sin(\theta/2)$, we obtain the form factor by summing over all created chains. Simultaneously the distance distribution function $h(r)$ can be calculated; $h(r)$ is related to $I(s)$ via:

$$I(s) \sim \int \mathrm{d}r\, h(r)\frac{\sin(sr)}{sr} \tag{17}$$

RESULTS AND DISCUSSION

Molecular dynamics simulations were performed for chains consisting of 15 monomers representing PPTA and PPIA at a constant temperature of 300 K. The coordinates of each atom were stored every 0.05 ps along a trajectory of 100 ps. Mean values were calculated using statistically independent data, i.e. sampling was performed according to the corresponding correlation times (for method (i) of the order of 0.1 ps, for method (ii) about 1 ps and for method (iii) about 2 ps). Analysis starts when the persistence length, being very high at the beginning of the trajectory, does not decrease any more (see *Figures 3–5*). The plot in *Figure 6* illustrates that the system was equilibrated after ~20 ps. The r^2 values fluctuate around a mean numerical value.

For PPTA three different initial conformations were simulated: one chain purely consisting of *trans–trans* conformations, one of *trans–cis* conformations and one of *cis–trans* conformations. As the most realistic chain a random occurrence of all possible monomeric

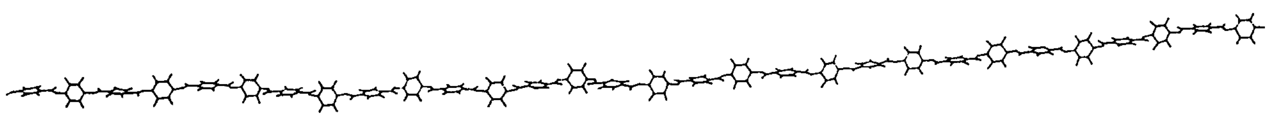

Figure 3 Snapshot of the molecular dynamics conformation after 0.5 ps

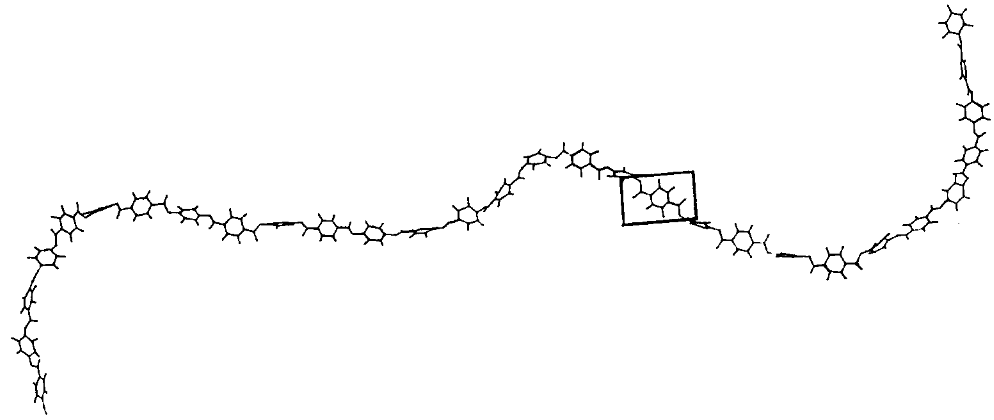

Figure 4 Snapshot of the molecular dynamics conformation after 20.0 ps. The marked residue is still in a *trans* position, but will soon switch into a *cis* position

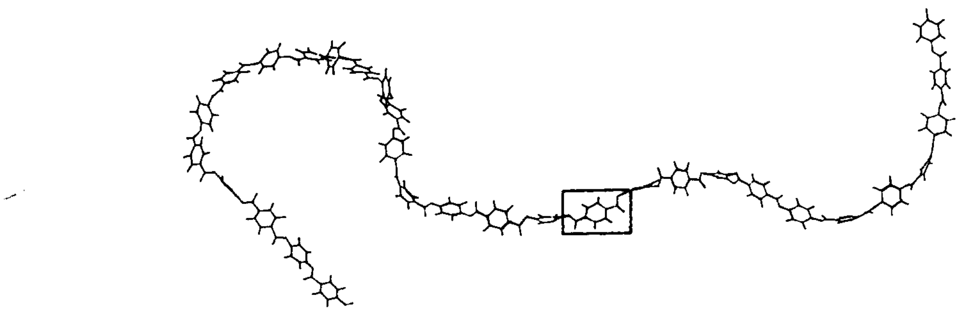

Figure 5 Snapshot of the molecular dynamics conformation after 60.0 ps. The marked residue is now in a *cis* position

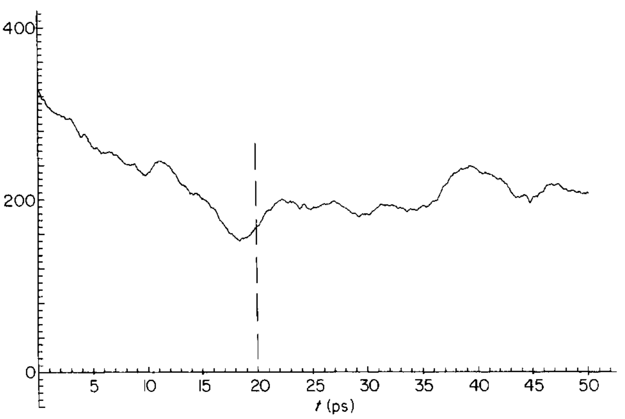

Figure 6 Plot of the squared end-to-end distance during the molecular dynamics simulation of $t = [0,50]$ ps. The broken line indicates the point where analysis of the trajectory was started

conformations including *cis–cis* conformations was assumed. The minimized potential energies for all of these four types of chains were almost equal, i.e. none of the chains has a particular preference for energetic reasons. For PPIA two different initial conformations were simulated, both with random occurrence of all possible monomeric conformations.

During the simulation (100 ps) only one change of a monomeric conformation was observed—in this case from a *trans–trans* conformation to a *cis–trans* conformation (see *Figures 4* and *5*). No ring flip occurred, in agreement with the low frequency of these events ($\sim 10^{-2}$/ns) as confirmed by n.m.r. studies[11]. studies[11].

Table 2 shows the average monomer length, mean bond and torsional angles and fluctuations for all simulated chains. These parameters are very similar for all PPTA chains and for both PPIA chains. Even by comparing PPTA to PPIA similar parameters are found, although fluctuations of angles tend to be lower for PPIA. The torsion of the phenyl ring in the hydroquinone residue with respect to the phenyl ring in the terephthalic acid was found to be 87.5° ± 14.1° for PPTA and 89.3° ± 13.5° for PPIA.

Table 3 shows the persistence length and related quantities for the 'random' chains calculated by the three methods described above. To prevent a strong dependence on the initial configuration of the PPIA chain we chose two different starting configurations, each of them consisting of the same percentage of *cis–trans* or *trans–cis* conformations respectively. The result for PPIA found by method (ii) is not really reliable, since $\langle \cos \omega \rangle$ in equation (12) gives to a large extent undefined arguments for the logarithm in (12). Generally the values for the persistence length calculated by all three methods agree very well with each other. Since method (i) only

Table 2 Mean length of a monomer, mean bond and torsional angles and fluctuations for PPTA and PPIA

PPTA	l'	$\langle\alpha_1\rangle$	$\Delta\alpha_1$	$\langle\alpha_2\rangle$	$\Delta\alpha_2$	$\langle\phi\rangle$	$\Delta\phi$	$\langle\gamma_1\rangle$	$\Delta\gamma_1$	$\langle\gamma_2\rangle$	$\Delta\gamma_2$
trans–trans	12.4	113.5	3.7	121.2	10.0	0.4	17.7	1.1	21.3	0.4	19.7
trans–cis	12.4	113.5	3.8	121.6	10.1	0.2	18.3	1.3	21.5	179.5	20.1
cis–trans	12.3	113.6	3.7	121.3	9.8	0.7	17.6	178.9	21.2	1.6	19.8
random	12.4	113.7	3.9	121.7	9.3	0.6	17.0	178.2 (1.8)	21.2	178.0 (0.9)	20.7
PPIA	l'	$\langle\alpha_1\rangle$	$\Delta\alpha_1$	$\langle\alpha_2\rangle$	$\Delta\alpha_2$	$\langle\phi\rangle$	$\Delta\phi$	$\langle\beta\rangle$	$\Delta\beta$		
random I	11.4	114.0	2.3	121.9	10.0	0.3	11.5	119.4	2.3		
random II	11.4	113.9	2.6	122.0	9.7	0.0	13.1	119.2	2.7		

Table 3 Persistence lengths (Å) for PPTA and PPIA

	Method (i)	Method (ii)	Method (iii)
PPTA$^{(u)}$	80 ± 2	78 ± 10	72 ± 10
PPTA	101 ± 4	105 ± 6	98 ± 14
PPIA/1	21 ± 1	23 ± 22	32 ± 10
PPIA/2	21 ± 1	18 ± 5	19 ± 5

$^{(u)}$ United-atom model

Errors are estimated in the following way: for method (i) the influence of the standard deviation of the cosine of the torsional angle of the ester bond on the standard deviation of the persistence length is considered; in method (ii) fluctuations of $\cos\omega$ (equation(12)) for different pairs of tangent vectors of the chain are regarded; and for method (iii) the influence of the uncertainty of $\langle r^2\rangle$ on the error of the persistence length is taken into account

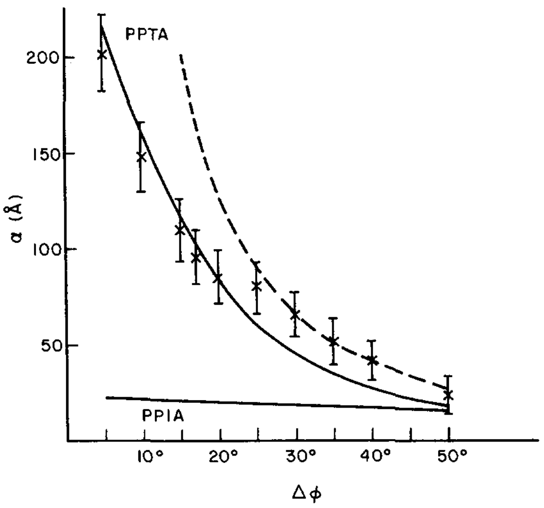

Figure 7 Dependence of the persistence length on the size of the fluctuations of the torsional angle around the ester bond for PPTA and PPIA. The data with error bars are calculated from chains generated by the Monte Carlo program. For each data point 500 chains consisting of 150 monomers were used. The full curves are calculated by method (i) varying $\Delta\phi$ while all other parameters are fixed. The broken curve has the analytical dependence given in the text. For PPIA it has practically the same shape as the full curve

takes local properties into account, while method (ii) and method (iii) use the entire conformation, the agreement of the results is an indication[12] that the performed simulation can be compared to a simulation under theta-point conditions, e.g. that the co-volume effect vanishes.

For PPIA the only comparison with experimental results for a polymer compound with similar behaviour is given for the liquid-crystalline terpolymer (LCP) consisting of residues HBA, HQ and IPA (*p*-hydroxybenzoic acid, hydroquinone and isopropyl alcohol)[15]. The authors claim LCP has a coil-like conformation in dilute solution. The value one obtains for the ratio $(\langle r^2\rangle/M)^{1/2} = A = 0.77$ Å g$^{-1/2}$ mol$^{1/2}$ agrees very well with our result for PPIA of $A = 1.1$–1.6 Åg$^{-1/2}$ mol$^{1/2}$.

For PPTA the result for the persistence length is in good agreement with experimental results for poly(phenylhydroquinone-*co*-terephthalic acid), which give a persistence length in the range of 60–150 Å[13]. The persistence length is larger than the one calculated for poly(*p*-hydroxybenzoic acid)(pPHB)[2] owing to the explicit consideration of the hydrogen in the present paper. To prove that the explicit hydrogens hinder rotations around the ester bond due to steric effects, we performed a calculation of the persistence length in the frame of the united-atom model (*Table 3*) for the PPTA. The fluctuation of the dihedral angle $\Delta\phi = 20.6°$ in comparison to $\Delta\phi = 17.0°$ for the all-atom model clearly causes a lower persistence length in the case of PPTA$^{(u)}$.

In the case of pPHB the dihedral angle fluctuation[2] was $\Delta\phi = 22°$ obtained within the united-atom model, which consistently explains the lower value of $a = 65$ Å for pPHB. The strong influence of these fluctuations on the dimension of the PPTA chain as well as the negligible influence in the case of PPIA is demonstrated in *Figure 7*. Assuming for a moment the approximation:

$$\begin{aligned}\langle\alpha_1\rangle &= \langle\alpha_2\rangle = \langle\beta\rangle = 120° \\ \Delta\alpha_1 &= \Delta\alpha_2 = \Delta\beta = 0\end{aligned} \tag{18}$$

the curves in *Figure 7* can be qualitatively described by an analytic expression for $\Delta\phi \ll 1$ calculated on the basis of equations (9) and (10):

$$\text{for PPTA} \qquad a \approx \frac{12.6}{2}\left(\frac{8}{3}\frac{1}{\Delta^2\phi} + 1\right)\text{Å} \tag{19}$$

$$\text{for PPIA} \qquad a \approx (21.6 - 3.6\Delta^2\phi)\,\text{Å} \tag{20}$$

The persistence length of PPIA is of the order of the persistence length of a flexible chain. Since the fluctuations for PPIA are the same as or even less than for PPTA and since in this sense the stiffness of both chains is about the same, it becomes obvious that for non-linear chains like PPIA the persistence length (or related quantities) is not a good measure for stiffness. We would like to point out here that the common definition of the persistence length in the RIS model as well as in the Porod–Kratky model takes the monomer length and intrinsic parameters like bonds, angles and their fluctuations into account. The widely used interpretation that a low persistence length characterizes

Table 4 Moments of distributions for fluctuations of a bond angle and a torsional angle compared to the moments for a Gaussian distribution

	$\langle X\rangle$	$\langle X^2\rangle$	$\langle X^3\rangle$	$\langle X^4\rangle$	$\langle X^5\rangle$	$\langle X^6\rangle$
Bond angle	0.00	1.00	0.01	2.95	−0.59	13.74
Torsional angle	0.00	1.00	0.12	3.18	1.21	17.73
Produced by an algorithm commonly used for creating normally distributed numbers[14]	0.00	1.00	0.00	2.90	0.00	13.52
Exact	0.00	1.00	0.00	3.00	0.00	15.00

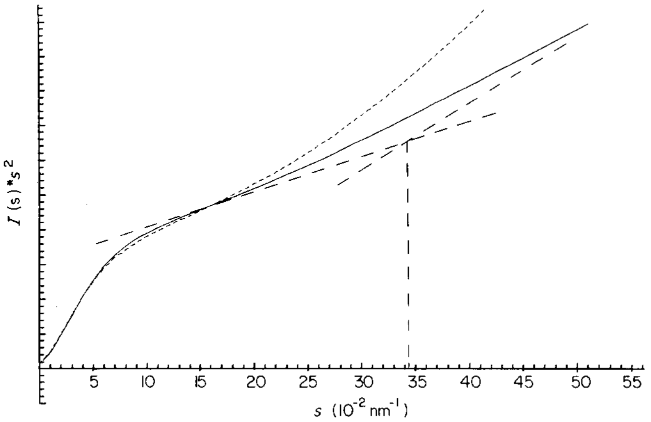

Figure 8 Kratky plot of the small-angle X-ray scattering form factor for a PPTA chain consisting of 150 monomers, averaged in this case over 1000 chains. The broken curve shows the result of an analytical calculation using the approach of Sharp and Bloomfield[17]. Input parameters for the contour length L and persistence length a are $L = 210$ nm and $a = 10$ nm. This result is valid for $s < 0.15$ nm^{-1} with an accuracy of 1%

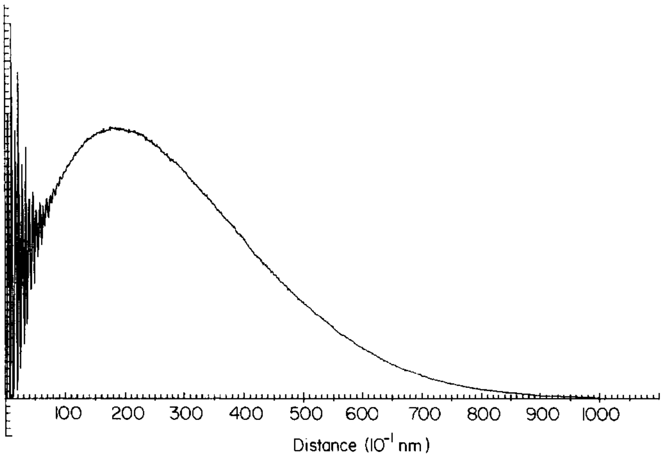

Figure 9 Distance distribution functions corresponding to the scattering form factor shown in *Figure 8*

a flexible chain has to be carefully examined in cases where the chain is not linear! It is recommended to look at the fluctuations of the torsional angle, as an intrinsic property that obviously determines the stiffness or the flexibility of a polymer chain.

Simulations of 'pure' PPTA chains give slightly higher persistence lengths of about 130 Å, but even the assumption of an equal mixture of *cis–trans* and *trans–trans* conformations leads to a value of about 100 Å for the persistence length. As a consequence this lower persistence length is not primarily caused by the occurrence of the *cis–cis* conformation and its specific geometry but by a fairly equal mixture of all conformations.

With the algorithm described above, a chain consisting of 150 monomers was created, using the parameters found in the molecular dynamics simulation for the 'random' PPTA chain and assigning equal probabilities for *cis* and *trans* positions. The assumption of a Gaussian distribution of the fluctuations was checked and confirmed to a very high degree (see *Table 4*).

Averaging over 500 chains gives for PPTA a persistence length of 96 ± 16 Å, in agreement with the results from the molecular dynamics. The form factor was calculated considering only the oxygen atoms as scattering centres in the first and sufficient approximation. Polydispersity was not taken into account. The form factor in terms of the Kratky plot (*Figure 8*) shows in a very nice way the typical features characterizing the transition from coil to rod scattering behaviour, namely a division into three parts: for small scattering vectors a part with a shape due to a Gaussian distribution of large distances within the chain, for large scattering vectors an asymptotic straight line through the origin and an intermediate part characterizing the transition. From this the persistence length can be estimated in two ways: following the procedure in ref. 16 gives:

$$a \approx (2.3/0.034)\,\text{Å} \approx 70\,\text{Å} \qquad (21)$$

while a fit to an analytical solution[17] using $a = 100$ Å as the input parameter gives a good agreement with the form factor. Both values are again in agreement with the molecular dynamics simulation, although for an exact determination of the persistence length even longer chains should be used.

The need for considering long chains becomes obvious when the corresponding distance distribution function is calculated. For a long chain the characteristic features of such a distribution are a maximum at about the mean radius of gyration, a Gaussian shape for long distances and sharp peaks for the monomeric distances within the order of the persistence length (*Figure 9*). For a smaller chain (20 monomers) the distance distribution function, which contains all information about the form factor (equation (17)), does not have a clearly distinguished maximum nor a Gaussian shape, and consequently the scattering form factor is not very structured (*Figures 10* and *11*).

CONCLUSIONS

Molecular dynamics trajectories on the atomistic level were used as input for three different models to determine the persistence length of PPTA and PPIA. It became clear that a distinction between linear and non-linear chains is necessary if one wants to judge the stiffness of a chain. An algorithm to create long polymer chains has been introduced. It has been shown that good statistics

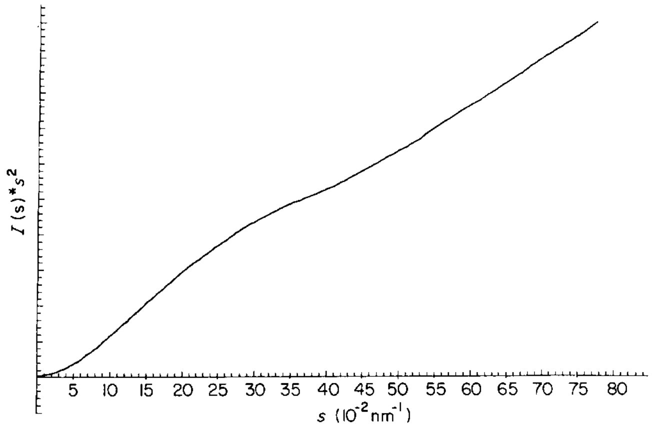

Figure 10 Kratky plot of the small-angle X-ray scattering form factor for a PPTA chain consisting of 20 monomers, generated by the algorithm described in the text

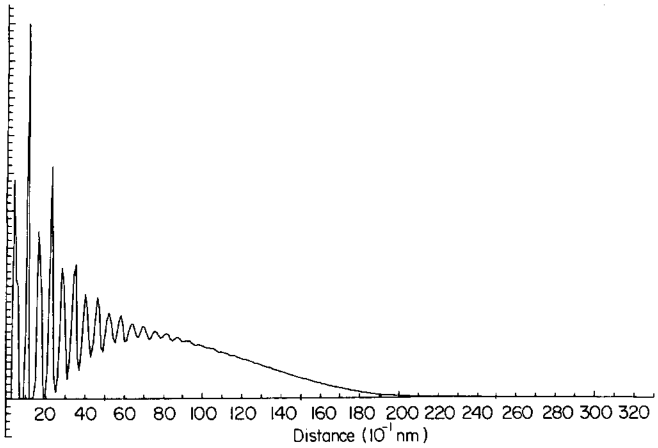

Figure 11 Distance distribution function corresponding to the scattering form factor shown in *Figure 10*

need to be created in order to calculate reliable form factors.

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